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The Metallurgist.

Supplement to The Engineer, *June, 1938.*

Magnetic Methods of Testing Materials.

THE greater part of a recent paper by W. Schirp,* dealing with magnetic methods of testing, is concerned with what the author terms the magnetic powder method of inspection of materials, more commonly known in this country as the ferrographic or magnaflux method. Some brief details of other magnetic and electrical methods are also given. Beyond a discussion of what may be called the mechanics of the powder method the paper contains little which is new and in some respects it is hardly up-to-date. It is, however, interesting as a record of experience with these methods in Germany. In any case the possibilities of these methods are not as widely known as their importance warrants.

The author discusses at some length the forces acting upon an iron particle introduced into the leakage field in the neighbourhood of a flaw in a magnetised specimen. The important force upon the particle is the "directing force" urging it towards the most intense parts of the field. This force, if it acted alone, would give accurate records, which could be easily interpreted, of the condition of the material. Unfortunately, this is not the only force acting. There is, in addition, a force due to leakage flux tending to make the particle adhere to the surface of the specimen at places where there is no definite flaw; friction may then prevent the particle moving towards a point where the field is more intense. Again, if the surface be inclined, gravity tends to prevent settlement where the field is strongest. To increase the general mobility the iron or iron oxide is suspended in oil or some similar liquid. Very much finer particles may then be used and, within limits, the method then becomes extremely sensitive. The author discusses the effect of the forces enumerated upon the sensitiveness of the method and, for certain hypothetical conditions, gives curves showing the limiting emergent flaws detectable under various intensities of magnetisation. Curves obtained under practical conditions would have been of interest. In any case emergent flaws are detected with great ease.

The use of an alternating magnetic flux, instead of a continuous flux, is discussed. It is pointed out that owing to skin effect an alternating flux is unsuitable for the detection of deep-seated flaws, but it is claimed that for fine surface flaws it is more sensitive since the leakage outwards from the surface is greater. The author does not remark upon the frequent "loss of definition" with an alternating flux and the advantage claimed is somewhat doubtful. The use of an alternating flux is usually decided by the practical consideration that big alternating currents can be obtained with greater ease than big direct currents. The combination of crossed direct and alternating fields, an arrangement which does often give a real increase of sensitiveness, is not mentioned.

The various methods of effecting magnetisation enumerated by the author are indicated in the diagram reproduced. In (*a*) the specimen is magnetised by being placed between the poles of a D.C. electro-magnet (the external D.C. method); the disadvantage is the difficulty of demagnetising the specimen after test. In (*b*) the specimen is magnetised by the passage of a big A.C. through it (the internal A.C. method); the magnetisation is chiefly confined to the surface. In (*c*) the hollow specimen is magnetised by the passage of a large A.C. through a conductor linked with it (the external A.C. method). In (*d*) the specimen is flash magnetised by D.C. and the remanent magnetism is used for flaw detection. In (*e*) the hollow specimen is flash magnetised by the passage of a momentary current through the conductor linked with it.

Flash magnetisation is attributed by the author to America. Possibly that is why he is apparently unaware of its possibilities with large specimens and of the apparatus used in that connection. The apparatus developed at the Research Department, Woolwich, permits of the application of the method to cylinders of considerable size.†

A number of practical applications of the magnetic powder method to engineering specimens are discussed by the author. With welds, deep-seated flaws and inclusions present difficulties, but fine cracks at or near the surface are easily shown. The method is particularly useful for the inspection of thin welded metal. It cannot be used for thicknesses in excess of 1 cm. For long seams a portable magnet is used. For the detection of surface flaws the internal A.C. method is recommended, a current of 100 amperes being used. No indication is given of the size of specimen for which this current is sufficient. For the inspection of rivet holes a copper conductor is placed in the hole and an A.C. of 300–500 amperes passed through it. For the inspection of the internal bore of tubes the external A.C. method is used with an ink spray and viewing apparatus. In this country the simpler method of flash magnetisation is used, which has the added advantage that viewing can be carried out clear of any obstruction.

Flash magnetisation is apparently used by the author only for small parts which can be dipped in the suspension after magnetisation. He refers to the use of batteries for supplying the heavy current required, but he himself prefers electrolytic condensers which are charged from the A.C. mains

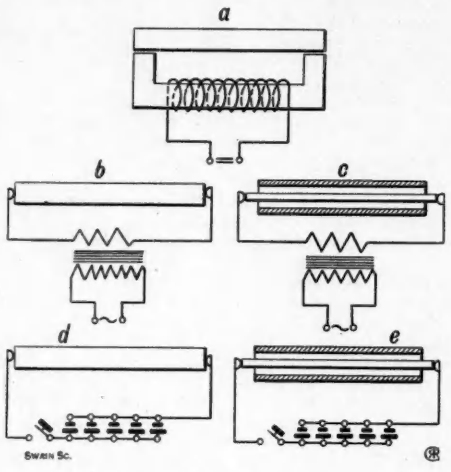
* "Results, New Possibilities and Limits of the Magnetic Method of Testing Materials," by Wilhelm Schirp, *Stahl und Eisen*, March 3rd, 1938, 58, 235-240.

† *Engineering*, Oct. 4th, 1935.

through rectifiers. More details of the actual apparatus employed would have been interesting; it is commonly found that if the circuit resistance is high the remanent magnetisation is small, because the current is not sufficiently great, and again, if the circuit resistance is low the remanent magnetisation is small, because the discharge is oscillatory.

The author recommends field strengths of the order of 50 ampere turns per centimetre, with which it is possible to detect easily the finest flaws provided they are not too far below the surface (*sic*). It is known that extremely fine flaws can be found by the method; the problem is to determine how far below the surface they may be and still be detectable. Some examples of hidden flaws are given which were afterwards disclosed by grinding, but there is no indication of the amount of metal ground off before the flaws were revealed.

Reference is made to the effect of stress upon this method of inspection. Spurious collections of the



Different Methods of Magnetising.

iron powder may occur at places where the surface has been pressed or bruised. The author shows that these markings may be avoided by the use of very intense magnetic fields. They are of magnetostrictive origin and they may be simply removed by the application of an A.C. electro-magnet.

The difficulty due to the extreme sensitiveness of the method to superficial flaws is discussed. Rejection due to flaws of no importance has to be avoided, though grinding cracks of very small depth may be serious in inducing fatigue in materials which may be subject to high alternating stress.

The importance of using the right intensity of magnetisation is emphasised. With this in view a comparator is described consisting of an iron disc in which a number of circular grooves have been cut. This disc is fixed to another disc of non-magnetic material and placed upon the specimen; both comparator and specimen are sprayed with the iron suspension. From the appearance of the disc it is said that the sensitivity to flaws of various depths can be estimated.

Very brief references to other magnetic and electrical tests are given. The chief disadvantage of the ferrographic method is its comparative insensitiveness to submerged flaws. Although the stray magnetic field emerging from a flaw may be insufficient to be indicated by the ferrographic method, it may still be detected by a rotating or oscillating coil. The Griesheim weld tester works upon this principle. Wire cables may also be tested by this method. In an apparatus illustrated the cable passes between the poles of a magnet and is encircled by a search coil. It closely resembles a tester designed many years ago by T. F. Wall. For non-magnetic materials Gerlach, in 1934, made use of the effect of flaws upon the eddy currents produced in the specimen by an alternating field (as did E. W. Marchant in 1926). A brief description is given of an apparatus based upon this principle and used for inspecting tubes and bars. It consists of four coils linking the tube or bar; two of these coils are supplied with A.C., two are connected in opposition and are used as detecting coils. With very uniform material such an elementary apparatus can be effective, but with much acceptable commercial material it fails to distinguish adequately between flaws and manufacturing variations of no importance. Far greater discrimination is afforded by the modified impedance method developed in the Research Department, Woolwich.‡

The ferrographic method of testing appears to be so extraordinarily simple to apply that it is far too often assumed that the results are equally easy to interpret and that its use requires no skill. That this assumption should gain acceptance is to be deplored, for it inevitably results sooner or later in some serious misinterpretation which, unfortunately, too often throws discredit upon the method rather than upon the user. A considerable part of a paper by H. Hänsel§ is concerned with the risks of misinterpretation, and it does not appear to have occurred to the author that many of the risks accepted might have been avoided. This paper and another which covers similar ground by F. Wever and H. Hänsel‖ are notable for the good series of pictures of specimens subjected to this test, rods of hardened tool steel, cold rolled bars, castings, and valve springs. All the specimens were small, and therefore there was no difficulty in magnetising them practically to saturation. Had the author extended his experience to large specimens, he might have obtained results which would have caused him to review his technique. So that flaws may be more easily detected, he recommends that specimens should be magnetised to saturation. Then, later, he remarks upon the difficulty encountered owing to the fact that all irregularities of permeability in the material are shown magnetically and may be interpreted as flaws. To him this fact and his technique appear to be unconnected. The magnetic markings shown on illustrated examples of drawn rods and valve springs would not be interpreted by an experienced operator as being due to flaws until further tests had been made with a lower degree of magnetisation and after magnetostrictive surface effects caused by working had been removed. That a high degree of magnetisation is necessary to detect subsurface flaws must be conceded, but surface flaws can be detected with but a small fraction of saturation. There is little objection

‡ *Engineering*, June 5th, 1936.

§ "Flaw Detectability and Magnetic Non-Destructive Testing." Heinrich Hänsel. *Archiv für das Eisenhüttenwesen*. April 1938, 1937-38, 11, 497-502.

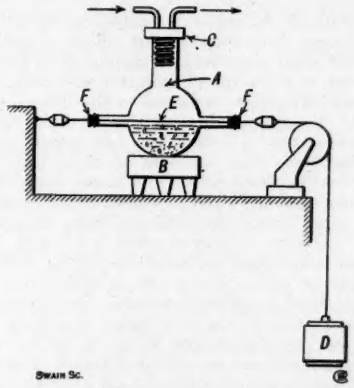
‖ "Contribution to the Magnetic Method of Testing Materials," by F. Wever and H. Hänsel, *Mett. K. W. Inst. Eisenforschung*, 1938, 20, 91-101.

to two tests when necessary. It has to be recognised that a certain degree of skill is required in applying the method; with experience the user is soon able to decide what evidence is acceptable.

The author gives a brief description of an apparatus developed in the Kaiser Wilhelm Institute for Iron Research for the magnetic testing of cylindrical bars and tubes. It consists of a D.C. magnet in the field of which the cylinder rotates at uniform speed. The field, the axis of the cylinder, and the axis of two detecting coils are mutually perpendicular. The two detecting coils are connected to a galvanometer. Irregularity in the specimen causes a deflection of the galvanometer. The apparatus appears to be but a simplification of one used many years ago by Dr. Burrows and his co-workers in America for the inspection of turbine discs. Judging by the refinements in construction which had to be adopted in that case, in order to avoid spurious effects, it is difficult to imagine how the present apparatus could detect any but gross defects. The author admits some difficulty due to irregularities in the thickness of walls of tubes. The advantage of such an apparatus, if it functions correctly, is, of course, that it can give some quantitative measure of a flaw.

Cracking of Steel in Ammonium Nitrate Solutions.

A REMINDER of the extreme readiness with which iron and mild steel will crack on exposure to hot ammonium nitrate solutions is given in a paper by M. Smialowski,[1] of the Technical High School, Warsaw. His work was initiated as a result of the occurrence of cracks in several iron girders of 0·16 per cent. carbon basic steel, which supported an



A, Pyrex glass apparatus; B, hotplate; C, reflux condenser; D, weight; E, wire specimen; F, corks.

FIG. 1—*Method of Testing Under Static Load.*

ammonium nitrate evaporating plant. The cracks, which were intercrystalline, occurred mainly at the most strongly deformed or stressed parts of the structure, especially round bolt holes.

In his experimental work Smialowski exposed stressed wire specimens of mild steel (Z) and of electrolytic iron (E) to the influence of hot 50 per cent. ammonium nitrate solution in an apparatus shown in Fig. 1, containing about 200 c.c. of the liquid. The mild steel, 1·2 mm. diameter, contained carbon 0·08, manganese 0·29, and copper 0·12 per cent., with other elements low; the electrolytic iron, 1·0 and 2·0 mm. diameter, was not of high purity, and contained carbon 0·005, manganese 0·08, chromium 0·08, nickel 0·03, and copper 0·05 per cent., with other elements low. The wires were about 5 mm. above the level of the solution, but when this was vigorously boiled, they were wetted over a length of about 10 cm. A device which recorded the duration of the experiment and cut out the heating current when the wire broke was included, so that the apparatus required no continuous supervision. A specimen, 30 cm. long, was stressed to just below the recorded yield point for 30 seconds and annealed in a gas flame. With precautions against bending, it was then threaded through the corks, as shown in Fig. 1, the grips were attached, and after the solution had been brought to boiling the weight D was applied and the timing device set in operation. The experimental data giving the time to fracture are contained in Fig. 2. The time was independent of the initial

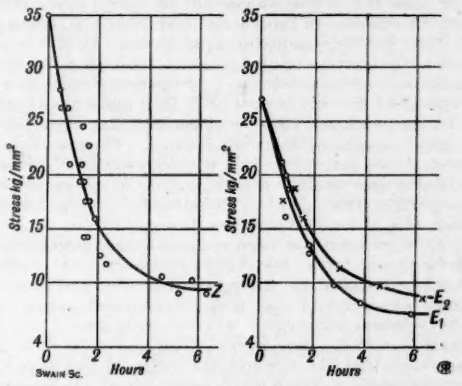


FIG. 2—*Time Required to Break Loaded Wire Specimens Exposed to Boiling Ammonium Nitrate Solutions.*

condition of the wire, whether slightly rusted or cleaned with fine emery. The failure in these thin specimens was very rapid under the requisite stress, the minimum value of which was :—

Specimen.	Stress.		Percentage of tensile strength.
	Kg./mm.²	Tons/in.²	
Z 1·2 mm.	9·5	6·0	27
E 1·0 mm.	7·0	4·5	26
E 2·0 mm.	9·0	5·7	33

Specimens which were not annealed after being stretched, or which were bent while being fitted in the apparatus, were found to crack in a very short time or at a very low load; for example, in such a specimen fracture occurred in two hours when the wire was loaded only to 4 kilos. per square millimetre (2·5 tons per square inch). The position of the cracks was revealed by bending the wire. They were found mainly in the parts of the wire lying in the side tubes of the apparatus or between these

and the centre, not at the position that received the maximum wash of the solution. Micro-sections showed them to be intercrystalline. The loss of weight of the wire by corrosion was very small; for example, when a specimen of the soft steel Z was broken under a load of 10 kilos. per square millimetre (6·35 tons per square inch), only about 0·04 grammes of iron passed into the solution and the sediment formed. Specimens loaded well above the yield point were unbroken when water replaced the ammonium nitrate solution.

The conclusion which Smialowski draws from these experiments is merely that it is dangerous to use soft iron in conditions of exposure to hot ammonium nitrate solutions. This, of course, has been very well known for a long time. He himself refers to Bosch [2] as being the first to make reference to the danger, and also to J. A. Jones's paper [3] in the Faraday Society's discussion on "The Failure of Metals under Internal and Prolonged Stress," but omits to mention the fairly extensive, though somewhat inaccessible, work of Swinden [4] on the subject.

The main interest of Smialowski's work lies in the fact that he endeavoured to assess the quantitative effect of stress in leading to fracture under the influence of ammonium nitrate solutions. He points out that the actual values are probably dependent on dimensions of specimen and other secondary factors, but this probably applies more to the time taken to fracture under a given load than to the minimum stress which must be applied before intercrystalline fracture is possible. It is quite clear that a certain minimum stress is essential, either externally applied or present as internal stress. The unstressed steel shows general surface corrosion, but no preferential intercrystalline attack, and no deterioration in properties (Swinden [4]). Smialowski's tests show that this stress is far below the yield point of the steel, whereas it has been suggested that permanent deformation was necessary (Jones [3]). A novel feature disclosed by the position of the fractures in these experiments was that intermittent action of the solution may have a more pronounced effect than complete immersion. The paper is also a reminder that the fundamental cause of this type of intercrystalline attack is still unexplained. It appears to be a specific effect of hot solutions of the nitrates of the alkali and alkaline earth metals. It is quite distinct from the corrosive attack of chlorides and sulphates. Its mechanism may be related to that of the cracking of steel in caustic solutions, but the same effective agent is unlikely to be produced from both types of solution. If, in the one case, it is hydrogen, it may, in the other, be nitrogen or a low oxide of nitrogen, as suggested by Swinden. This work links up with the important investigations of W. C. Schroeder, A. A. Berk and R. A. O'Brien,[5] which, although mainly devoted to caustic solutions, deals at some length with cracking in nitrate solutions also. Their conclusions were that intercrystalline cracking is produced by a solution which tends to form a protective film over the crystal surfaces while it attacks the grain boundaries. They suggest that the intercrystalline corrosion may be accelerated by electrochemical potentials existing between the protected crystal faces and the grain boundaries, as well as by the presence of hydrogen depolarisers. Progress of the crack may be enhanced by bursting forces existing within the grain boundaries if the corrosion products occupy a greater volume than the iron itself. This in particular is thought to apply to the action of nitrate solutions. No explanation, however, is yet fully supported by experimental evidence.

REFERENCES.

[1] *Korrosion und Metallschutz*, March-April, 1938, 14, 111.
[2] *Zeit. Elektrochem.*, 1918, 24, 361.
[3] Trans., Faraday Soc., 1921, 17, 102.
[4] Birmingham Metallurgical Society, 1923; *Iron and Coal Trades' Review*, 1923, 106, 220.
[5] *Metals and Alloys*, November, 1937, 8, 320.

The Rate of Corrosion of Copper-Bearing Steels in the Atmosphere.

THE study of the corrosion of copper-bearing steels goes back more than a quarter of a century; the bibliography is now very extensive, and it has become generally recognised that the balance of the evidence is in favour of the beneficial effect of small copper additions under conditions of atmospheric exposure. It has been difficult, however, to arrive at a sound estimate of the quantitative effect of copper, though the extensive series of tests being carried out by the Iron and Steel Institute Corrosion Committee are proving valuable. Up to the date of publication of the Committee's fourth report (1936) the tests showed that the improvement in the atmospheric corrosion resistance of steel by the presence of copper is of the order of up to 30 per cent., and that only about 0·2 per cent. of copper was required to produce the maximum effect. Some indications have been obtained that the beneficial effect of copper increases with the time of exposure of the steel, but the evidence is not fully conclusive. One exception was met with, namely, that with exposure in the highly polluted atmosphere of certain railway tunnels where the metal is protected from rain, the copper appeared to have no effect. Thus it seems possible that the effect of copper may vary to some extent with the service conditions of the steel.

The bulk of the other published work on copper steels having been carried out under a variety of conditions with materials of various descriptions, it is difficult to draw direct comparisons owing to the absence of standards common to the different series of tests. Thus, in evaluating the effect of copper, it is advantageous to employ a statistical method. Work has been done recently on these lines by K. Daeves and K. Trapp (*Stahl und Eisen*, 1938, 58, 245), which merits careful study. These authors have taken all the more important published data on the atmospheric corrosion of carbon steels (excluding marine conditions), and have included the results of an extensive series of tests of their own and also those of the Iron and Steel Institute Corrosion Committee. The data thus referred to a wide range of steels of which the copper content ranged from traces to 1·14 per cent. (overall mean 0·20 per cent.) and the phosphorus content varied from 0·002 to 0·55 per cent. (overall mean 0·06 per cent.). The test results, amounting to some hundreds, were calculated where necessary to a common basis of average penetration in millimetres per year. First, all the values, irrespective of the composition of the steel or of the atmospheric conditions of the exposure, were plotted, the abscissæ showing rate of corrosion in millimetres per year and the ordinates showing the number of times a particular corrosion rate was found among the test results. The "frequency curve" produced (Fig. 1) showed two peaks corresponding to rates of corrosion

of 0·05 mm. and 0·073 mm. per year. The secondary peak in Fig. 1 was attributed mainly to the influence of values for urban and country exposure, as a second graph (Fig. 2) drawn in a similar manner, but allocating the test results into three groups

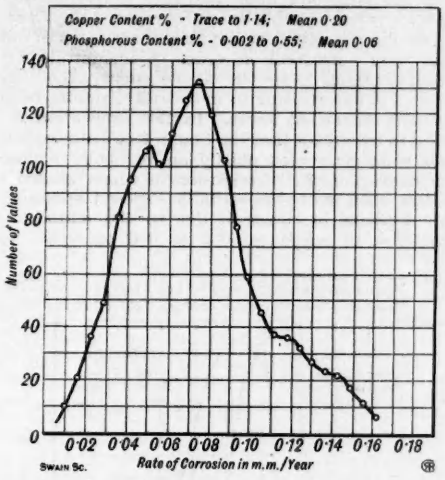

Copper Content % - Trace to 1·14; Mean 0·20
Phosphorous Content % - 0·002 to 0·55; Mean 0·06
Number of Values
Rate of Corrosion in m.m./Year
SWAIN Sc.

FIG. 1—*Frequency Curve of the Corrosion Rates of Steels Obtained in all Known Investigations.*

according to the general type of corroding atmosphere, gave three curves showing as chief features maxima of 0·073 mm. per year (industrial atmosphere), 0·05 mm. per year (urban atmosphere), and 0·035 mm. per year (country atmosphere)

	Industrial Atmos.			Urban Atmos.			Country Atmos.		
	From	To	Mean	From	To	Mean	From	To	Mean
Copper Content %	Trace	1·14	0·19	0·008	0·26	0·11	Trace	1·14	0·26
Phosphorous "	0·002	0·55	0·064	0·004	0·10	0·039	0·005	0·24	0·041

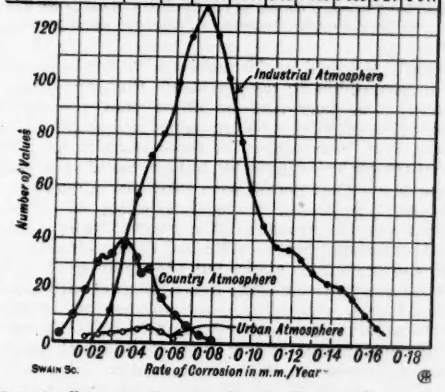


FIG. 2—*Frequency Curve as Fig. 1; Separate Curves for Industrial, Urban and Country Atmospheres.*

respectively. These maxima, representing the most frequently occurring values in the three categories of corrosion conditions were termed "normal values." An inference which may be drawn is that these are the most probable corrosion rates under "typical" conditions for steel of the composition represented by the average composition of the steels tested, which is that of a copper-bearing steel.

In separate tests carried out by Daeves, it was found that in an industrial atmosphere the rate of corrosion of steel wires remained substantially constant from year to year over an eight years' test period. On the other hand, with similar steels exposed for the same period in a country atmosphere, the rate of corrosion slowed down as the test proceeded. This varying rate of corrosion means that in order properly to compare the corrosion rate of different steels exposed in a country atmosphere, the comparison must be based on the same period of exposure. Now the results assembled in Fig. 2 were obtained over test periods varying in the different tests from five to ninety-seven months, most of them being over a year in duration. Therefore, Daeves and Trapp recalculated these results, determining the average rate per year at which the steels would have corroded had the tests been all continued for eight years, and had the rate of corrosion decelerated to the same extent as in Daeves' separate country air tests. A

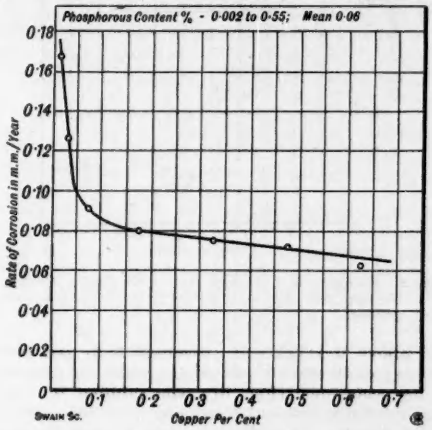


FIG. 3—*Variation of Corrosion Rate with Copper Content in Industrial Atmospheres; Values Obtained in all Known Investigations.*

new frequency curve was thus obtained, the smoothness of which appeared to confirm the reliability of the calculated data; its maximum (0·018 mm. per year) was considerably lower than the maximum (0·035 mm. per year) of the corresponding uncorrected curve in Fig. 2, and was considered to furnish a more accurate "normal value" for country air exposure. It may also be noted that the normal country air value of 0·018 mm. per year corresponds with an average steel composition of copper 0·26, phosphorus 0·042 per cent., whilst the normal industrial atmosphere value of 0·073 mm. per year (Fig. 2) refers to an average steel composition of copper 0·19, phosphorus 0·064 per cent. As steels of these two compositions would be expected to have very closely similar corrosion rates under the same conditions, these normal values for country and industrial atmospheres respectively were held to give, in effect, a direct relationship between the corrosion rates of the same steel under the two typical conditions.

In order to determine the general trend of the existing data regarding the effect of copper content, the arithmetic mean of the rate of corrosion for all steels of the same copper content was plotted against the percentage of copper. The curves obtained for exposure in industrial atmospheres (Fig. 3) and

country conditions (Fig. 4) were similar in type and showed that the corrosion resistance rose rather sharply with copper content up to 0·15 per cent., but did not increase very much with larger amounts of copper. Another method adopted was to assemble the data on rate of corrosion into two groups respectively relating to steels with copper contents up to and including 0·1 per cent. (average 0·04 per cent.)

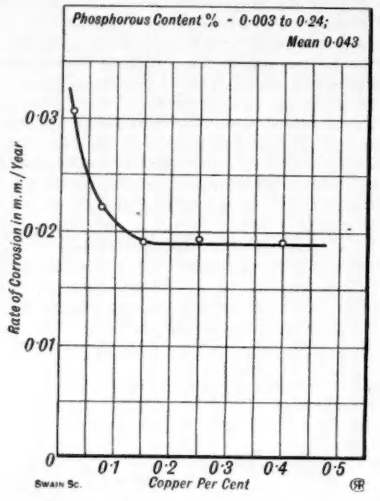


FIG. 4—*Variation of Corrosion Rate with Copper Content in Country Atmospheres; Values from all Known Investigations.*

and above 0·1 per cent. (average 0·27 per cent.), and to plot the rate of corrosion against the frequency of its occurrence (Fig. 5); the number of results available only justified this being done for industrial atmospheres. According to the curves obtained, the "normal" rate of corrosion of the lower copper group was 0·027 mm. per year greater than the "normal" value of the higher copper group.

The main statistical results which emerged from the above survey regarding the effect of copper were as follows:—Steels with 0·2 per cent. of copper corrode at the rate of about 0·075 mm. per year (0·003in. per year, 600 g. per square metre per year) under industrial atmospheric conditions, and at about 0·020 mm. per year (0·0008in. per year, 150 g. per square metre per year) in country air; the value for urban exposure lies in between these values. Steels with 0·02 per cent. of copper corrode at the rate of about 0·150 mm. per year (0·006in. per year, 1200 g. per square metre per year) under industrial conditions, and at about 0·030 mm. per year (0·0012in. per year, 250 g. per square metre per year) in country air. Industrial air is about four times as corrosive as pure country air. Increase of copper content from 0·02 to 0·2 per cent. reduces the rate of corrosion to approximately one-half. Relatively little improvement is secured by increasing the copper content above 0·15 per cent. Compared with steels containing 0·05 per cent. of copper, steels with 0·15 per cent. of copper corrode in the atmosphere at about a 20 per cent. slower rate. It was concluded that the use of copper-bearing steel is of considerable importance economically. Thus, it was estimated that if all steelwork employed in the unprotected condition, or steelwork not protected by periodical repainting, such as galvanised structures, were of steel containing at least 0·15 per cent. of copper, the reduction in the yearly loss by rusting in Germany alone would amount to 20,000 tons.

In the Iron and Steel Institute Corrosion Committee's recently published fifth report (May, 1938) the results presented for the rate of corrosion of mild steel were consistent in order of magnitude with those emerging from the above survey, the Committee's values relating to industrial exposure being, however, somewhat lower. In this connection it is useful to remember that the Committee's atmospheric tests were conducted chiefly on vertically exposed specimens, the rate of corrosion of which tended to be less than with horizontally exposed specimens. The decrease in corrosion due to the addition of quantities of copper of 0·2 to 0·5 per cent. was

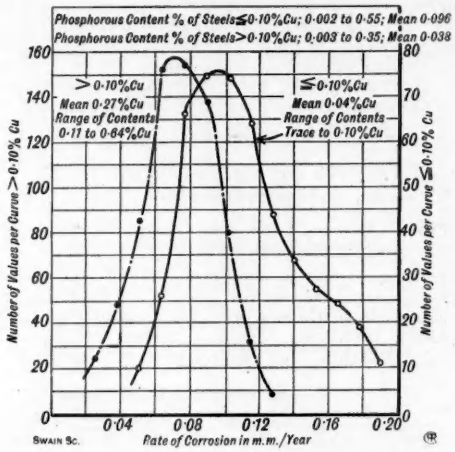


FIG. 5—*Frequency Curves of the Corrosion Rates of Steels with Different Copper Contents in Industrial Atmospheres.*

roundly assessed at 30 per cent., a figure which is less favourable to copper steels than the German survey. It may also be noted that the rate of corrosion of mild steel remained substantially the same from year to year for three years in an industrial atmosphere (Sheffield), but decreased appreciably over a five-year period with exposure in country air (Llanwrtyd Wells), a peculiar effect of location similar to that brought out in Daeves' tests

This account has been limited to the consideration of copper content alone, but the study of the effect of various other elements in conjunction with copper, phosphorus, chromium, and silicon, for example, is broadening out into a wide field of investigation and development of low alloy steels which promise further increase in corrosion resistance

Deposition of Tin from the Vapour Phase.

A NEW process for coating brass, copper, iron, zinc, and other metals with tin has been worked out by Dr. B. W. Gonser and Mr. E. E. Slowter, of the Battelle Memorial Institute, and described by them

in a paper* on "The Coating of Metals with Tin from the Vapour Phase." The method, referred to as "Stannising," is applicable to fabricated articles of the most complicated shapes.

The articles to be treated are freed from grease with soap and water, or by means of a solvent, and suspended at 500 deg. to 600 deg. Cent. for a few minutes in an atmosphere of hydrogen and the vapour of stannous chloride. A quantitative study of the reaction showed that in contact with the metal surface the hydrogen reduces the stannous chloride to tin according to the equation

$$SnCl_2 + H_2 \rightleftarrows Sn + 2\,HCl.$$

The tin is produced by reduction and not by replacement in the chloride. It is deposited as pure tin on the surface of the material to be coated. Since it is molten and at a temperature sufficiently high for an alloying action to take place with most metals, the tin does not long remain pure unless the rate of deposition is much greater than the rate of diffusion. The coating thus consists largely of a tin alloy of composition dependent on the factors governing diffusion, *i.e.*, temperature, time, and character of the basis metal. With copper as the basis metal, the character of the surface varies with the temperature of exposure to the vapour. The lower the temperature of treatment, the richer in tin will the surface layer be, and the higher the temperature the richer in copper, on account of the greater progress of diffusion. Many of the tin-copper alloys are very hard, and, in consequence, wear resistance far in excess of that obtainable with pure tin appears possible. A bright hard reflecting surface of speculum metal can also be obtained. Coatings can be applied to rough, threaded, or irregular surfaces; and machine parts can be built up to size again after first machining slightly to undersize.

Coatings on steel are hard and brittle, since they consist largely of a tin-iron compound. The hot water test† shows some degree of porosity in these coatings, but less than is present in ordinary tin-plate.

When tin does not alloy with the basis metal, a rough or incomplete covering is obtained, since the deposit tends to collect into irregular droplets, owing to surface tension of the molten tin. Tin is not deposited by this method on glass or refractory materials. Occasionally, however, droplets of tin are noted on ceramic materials at a few points where it is suspected that local impurities are reduced to metal by the hydrogen atmosphere. Apparently a metal surface is needed to activate the decomposition of the volatilised tin compound. The presence of a metal which alloys readily with tin appears to be desirable to obtain a smooth coating by wetting the metal surface, but it does not seem essential to the reaction since the rate of deposition is not diminished as the metal surface becomes coated.

From a commercial standpoint, stannising shows promise of advantage over other coating methods in producing even coatings of tin alloys over the internal and external surfaces of irregularly shaped articles. Its field of utility is probably in coating articles which are benefited by a coating of tin alloy rather than of pure tin. Interesting possibilities are opened for producing very hard or unusual alloy coatings by this method.

* Technical Publication A.76 of the International Tin Research and Development Council.

† D. J. Macnaughtan, S. G. Clarke, and J. C. Prytherch, *Journal*, Iron and Steel Inst., 1932 (1), 125, 159.

Measurement of Surface Stress by X-Rays.

SOME years ago attention was directed in these columns to a paper by Sachs and Weerts,[1] in which experiments were described by means of which the elastic stress in the surface of a bent bar of duralumin had been measured. It was stated on that occasion that the application of these methods to other materials would lead to important results. The intervening years have seen so great an improvement in the technique of X-ray measurement of high precision, which is necessary for the method, that it is now available for purposes of test or inspection of the products of a factory. Before proceeding to discuss some recent communications on this subject, it will be advisable to describe briefly the fundamental ideas involved. The method consists essentially of an application of the "back reflection" method so frequently used for accurate measurement of crystal lattice parameters. A beam of X-rays X O, Fig. 1, confined by a slit S, falls on the specimen at O,

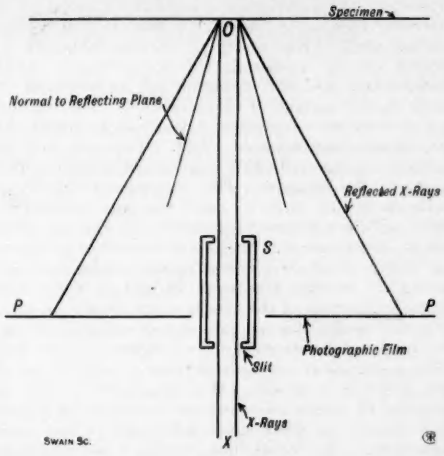


FIG. 1—*Diagram of "Back Reflection" Method, Showing Selective Action of X-ray Beam.*

and after reflection is recorded on the photographic film P P. The angle 2 θ between the incident and reflected beams is fixed by the wave length of the X-rays employed and the spacing of the planes of atoms in the crystal which produce the reflection. When the wave length is chosen so that some crystal plane produces a reflection at a value of 2 θ approaching 180 deg. the distance P P which is a measure of 2 θ, is very sensitive to small changes in the crystal parameter. The sensitivity is so great that the changes in interatomic distance produced by external loads applied to the specimen can not only be detected but measured with a considerable degree of accuracy. The simplest case which can arise is when the specimen is subjected to a deformation which produces a tension s at O in Fig. 1. This will produce a lateral contraction $e = \nu s/E$, where ν = Poisson's ratio and E = Young's modulus for the material. The strain e can be measured by the X-ray method, and if the elastic constants E and ν are known the stress s can be evaluated. Alternatively, if the stress is known the elastic constant E/ν is found.

A number of experiments have been carried out by H. Möller and J. Barbers[2] in recent years with the object of testing the accuracy of the method. They found that the value of the elastic constant E/ν for iron was 60,000 kilos. per square millimetre from their X-ray measurements, while the value found by direct mechanical tests was 75,000 kilos. per square millimetre. The difference is well outside experimental error, and must be attributed to the assumptions implicit in the calculation of the strains which will be produced by a given stress distribution. That a calculation carried out on the lines indicated in the preceding paragraph can only be expected to yield an approximate value for the elastic modulus can be easily seen. The example as given is, of course, greatly over-simplified, but, in addition to this shortcoming the X-ray method does not measure quite the same quantity as the direct mechanical test. When Young's modulus is determined by a tensile test on a bar of iron the experimental method averages the effect of the stress on all the minute crystals which constitute the specimen. The X-ray beam, on the other hand, selects those crystals which are so orientated that they satisfy Bragg's law, connecting the wave length with the spacing of the reflecting planes, and measures the strains in these crystals only. The group of crystals selected will depend on the material, the wave length of the X-radiation, and the direction of incidence of the beam on the surface of the specimen. For instance, in Fig. 1 where the incident beam is perpendicular to the surface, the crystals which reflect all have the normals to the reflecting plane inclined at a fixed angle to the surface. The mechanical and X-ray methods do not really measure the same quantity, so that until due allowance is made for this fact the results cannot be compared. There is still another complicating factor of which account must be taken in comparing the results of mechanical and of X-ray tests. In the evaluation of the elastic modulus of a specimen from the results of a mechanical test it is assumed that the material behaves like an isotropic elastic solid. This assumption is experimentally verified for the test piece as a whole. We say, in fact, that the material of which the specimen is composed behaves as if it were the ideal elastic solid with certain elastic constants. The metal, however, is a polycrystalline aggregate, and although it may in bulk display the properties of an isotropic solid we cannot assume that the individual crystals are themselves isotropic. That the effect of anisotropy is appreciable has been shown by Möller and Barbers, who have found that the difference between the values of the quantity E/ν for iron determined by X-ray and mechanical methods is reduced to about 8 per cent. when account is taken of it. In obtaining this result, use was made of the elastic constants of single crystals of iron, determined by E. Goens and E. Schmidt, and it was assumed that each crystal of the aggregate behaved independently of its neighbours and deformed according to the orientation of its crystallographic axes to the principal stresses. Although the assumption as to the mutual independence of the crystals is open to objection, their work has effected a considerable improvement in agreement between the results of the two kinds of experiment.

Recently, H. Möller and G. Strunk[3] have described a series of experiments in which the theory has been tested. The X-ray method has been applied to the evaluation of the elastic constant E/ν for steel subjected to tensile and to flexural stresses. The experimental work includes oblique incidence of the X-ray beam, the introduction of which is stated to be due to Glocker and his collaborators, and renders possible the investigation of biaxial stresses. The mathematical analysis is too complex to be followed here, but the result is to show that reasonable agreement with mechanical tests is obtained when proper account is taken of the elastic anisotropy of the iron crystals, in the case of normal incidence; for the cases of oblique incidence examined the inclusion of the corrections arising from the elastic anisotropy of the crystal is not necessary. To illustrate the scope and accuracy of this investigation there is reproduced in Fig. 2 the experimentally determined stress-parameter curve, for a steel in flexure. The composition of the steel is carbon, 0·23; silicon, 0·23; manganese, 0·50; phosphorus, 0·01; sulphur, 0·02; nickel, 2·75; chromium, 0·78 per cent. As the stress is increased the lattice parameter decreases linearly up to 65 kilos per square millimetre, the yield point of the material, when no further change of the parameter takes place. On removal of the stress the lattice parameter increases again, but does not revert to its initial value because the metal is now self-strained as a result of the plastic deformation at the highest stresses imposed. A series of lines of the type illustrated is obtained under a variety of experimental conditions, the direction of incidence, the composition of the steel, and the type of loading all being varied. The slopes of these lines are then compared with the slopes calculated from the mechanically determined elastic modulus with and without the assumption of elastic isotropy. For normal incidence of the X-ray beam the mean value of the slope is $-4{\cdot}11 \times 10^{-5}$ mm.² Å/kg.; the calculated slope taking account of anisotropy is $-4{\cdot}22$ in the same units, while if the correction for anisotropy is neglected the slope should be $-3{\cdot}88$. Although the effect of the correction is rather small the experiments indicate that it is observable.

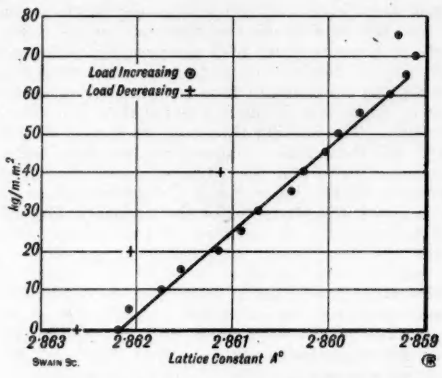


FIG. 2—*Load-Lattice Constant Diagram for Steel in Flexure.*

The X-ray method of determining stress can be used for test or inspection of finished products. For this purpose the calculation of the stress is not essential. The strain in the surface can be directly measured without destroying the material on which the test is being carried out, and for many purposes it would be sufficient to know that the strain did not exceed some critical value. Some interest attaches to the examples of this use of the method which are described in a paper by H. Möller and A. Roth.[4] These authors have applied the method to the investigation of the stresses in a welded triangular frame-

work and in a rolled duralumin tube. The welded structure is illustrated in Fig. 3, taken from the original paper; the numbered circles on the photograph refer to the places examined by X-rays. Reference to the original paper will show that an exhaustive examination of both sides of the framework was made, but for the purpose of illustrating the sort of result obtained in the investigation a description of the part shown in the reproduction will suffice. The accompanying Table I contains the

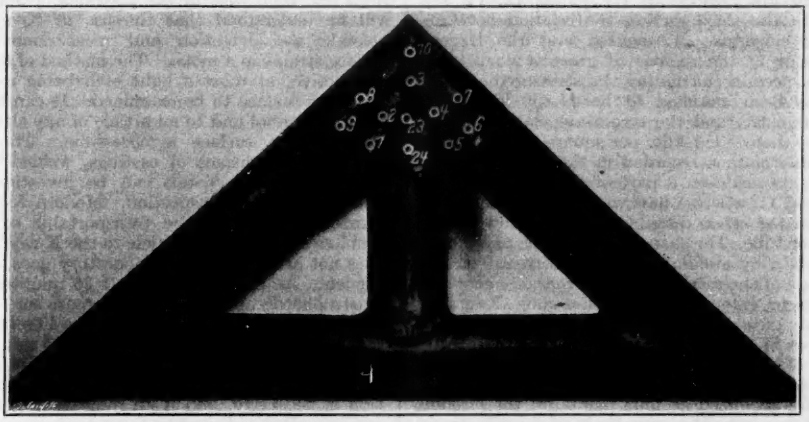


FIG. 3—*Welded Triangular Framework of Chromium-Molybdenum Steel Tubes (front view).*

TABLE I.—*Surface Stresses in Triangular Frame of Chromium-Molybdenum Steel.*

In weld seam $a_0 = 2 \cdot 8619$ Å.		Stress, kg./mm.²	In tube $a_0 = 2 \cdot 8610$ Å.		Stress, kg./mm².
Region of Fig. 3.	a.		Region of Fig. 3.	a.	
1	2·8602	+36	6	2·8615	−11
2	603	+34	7	606	+ 8
3	603	+34	8	598	+25
4	603	+34	9	618	−17
5	604	+32	23 not measurable		
10	611	+17	24	628	−38

\+ indicates tensile stress.
− indicates compressive stress.

figures corresponding to the regions subjected to analysis; inspection of the figures shows that in the weld the metal is in tension, while in the neighbouring parts of the tube the stresses are both positive (tension) and negative (compression), the distribution of these stresses being more or less random. In the original text thirty-four observations on different regions of the frame were made and those made on the seams all gave a tensile stress; the stresses in the tube near the welds varied between ±38 kilos. per square millimetre with a mean compressive stress of 8 kilos. per square millimetre. The above figures refer to a structure made of a chromium-molybdenum steel tube. Somewhat similar results were obtained from a similar frame constructed of a carbon steel, the stresses on the whole seem to be rather smaller than in the chromium-molybdenum steel; in the seams the stress varies between a tension of 23 kilos. per square millimetre and a compression of 11 kilos. per square millimetre, with a mean tension of 6 kilos. per square millimetre. In the tube the stress is compressive with a mean value of 12 kilos. per square millimetre.

In the same paper a further example of the evaluation of surface stress is given in a description of an investigation of a rolled duralumin tube. The tube was examined in three sections, the forms of which are shown in Fig. 4; the sections were separated by distances of about 8 cm. measured along the tube. The points examined are indicated by numbers

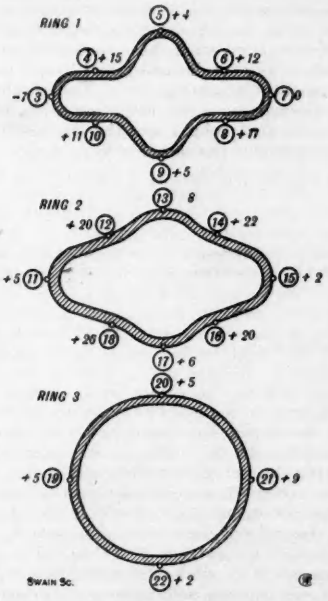


FIG. 4—*Stress Distribution on Three Sections of Duralumin Tube*

enclosed in circles, and the stresses found at these points are shown on the drawing, + indicating tension and − compression. It will be seen from the figure that the stresses in the first section lie between −7 and +17 kilos. per square millimetre,

the smallest tension (0) and largest compression (−7) occurring at the points 3 and 7 where the curvature is greatest. In the slightly less curved parts 5 and 9 the tensions are a little greater, and are greater still at the other four points where the section is flat. A similar result holds for the second section where the tensions are greatest at the points 12, 14, 16, and 18. In the third section the relation between stress and curvature is reversed and the largest stresses occur at the regions of greatest curvature. For the purpose of calculating the stresses the value of E/ν has been assumed to be 21,800 kilos. per square millimetre, and the errors are claimed to be not greater than $\pm 1 \cdot 1$ kilo. per square millimetre.

Other observations recorded in the paper refer to measurements made on a part of the tube, between points 3 and 11, where a flaw was visible. Some disturbance of the stress distribution was found in this region of the tube. The change of stress due to removal of the surface by etching was also investigated.

The scope of the method of stress measurement has recently been extended by Glocker and Kemnitz[5] to the study of fatigue failure. The tests were carried out on a bar of steel in which a radial hole of half the diameter of the bar had been drilled. Under the influence of an applied torsional load stress concentrations are produced at four points on the circumference of this hole, the magnitude of the stresses in these regions being about four times larger than those in a similar bar without the hole. One of the regions of stress concentration was subjected to X-ray examination while the specimen was undergoing an alternating torsional test. In order to obtain a photograph at the instant when the strain was at a maximum, the X-ray camera was fitted with a shutter synchronised with the frequency of the testing machine. The strains measured in the alternating test were compared with those measured in a static test in which the torque was equal to the maximum applied in the alternating test. The results of the test are summarised in the following table, where the figures in the first column are the stresses developed in the bar without the radial hole.

TABLE II.—*Static and Alternating Stresses at the Edge of a Perforation.*

Load increments, s_o, kg./mm.²	No. of cycles, millions.	Static s_{max}, kg./mm.²	Alternating s_{max}, kg./mm.²
4·55	4·5	17·7	18·2
5·3	10	20·6	20·8
6·3	0·5	25·8	25·1
(crack	develops)		
6·3	12	17·0	17·5

The figures in the last two columns show that the stresses developed by static and alternating loads are virtually identical, the small differences being within the limits of experimental error, and the increases recorded are directly proportional to the increments of stress in the first column. In the first column the ratio of the values of s_o is $1 : 1 \cdot 17 : 1 \cdot 39$, while for s_{max} the ratio is $1 : 1 \cdot 15 : 1 \cdot 38$. After the development of a crack the stress falls from 25 to 17 kilos. per square millimetre, the presence of the crack being confirmed by etching the specimen. This feature of the investigation is of considerable interest and may prove ultimately to be of practical importance as a method of detecting invisible surface flaws. At the moment this application of X-ray investigation can hardly be said to have emerged from the laboratory stage of development, but it suggests that more will be heard of it in the study of problems connected with fatigue failure.

In conclusion, it may not be out of place to make one or two brief remarks of a general nature concerning the utility and applicability of the X-ray method as a practical method of test and inspection. From what has been said in the preceding paragraphs, it will be understood that the use of X-rays makes possible the detection and measurement of the surface strains in a metal. The method of test is non-destructive, at most a light etch being required to clean the surface to be examined. It can be applied to any material and to an article of any size or shape provided the surface is accessible. The state of strain in the surface of castings, welded structures and cold-worked metals can be investigated as a routine method of inspection. Modern X-ray equipment is designed to be transportable so that the problem of getting the article to the X-ray laboratory does not arise, the X-ray laboratory goes where it is needed. An exposure of about 30 minutes will produce a photograph and for the purpose here considered measurement of the position of one line of the spectrum is all that is required in order to find the strain in the material, assuming that the spectrum of the unstrained material is known. No lengthy calculation is necessary, and if an indication of absence of strain is all that is required, comparison of the photograph with a standard obtained from strain-free material will suffice.

In some respects the method may be compared with the use of polarised light for the investigation of stresses in structures, but it is directly applicable, and the results do not have to be deduced by extrapolation from experiments on a transparent medium. Moreover, it is the surface strains, so potent a cause in the initiation of fracture, that are now made susceptible to detection, and therefore to control, and by improved design to elimination.

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[2] *Mitt. Kais.-Wilh.-Inst. Eisenforsch.*, 1934, 16, 21; *ibid.*, 1935, 17, 157.
[3] *Ibid.*, 1937, 19, 305.
[4] *Ibid.*, 1937, 19, 123.
[5] *Zeit. für Metallkunde*, 1938, 30, 1.
Reference may also be made to "Internal Stresses," a review by Charles S. Barrett, Carnegie Institute of Technology, Contribution 48, 1934. This review, which appeared in *Metals and Alloys*, 1934, pages 131, 154, 170, 196, and 224, covers both mechanical and X-ray methods of tests. Over 100 original papers are referred to.

The Effect of Superheating Molten Steel.

ATTENTION is directed to the probable importance of the effect of superheating in steel making in a paper on "Effect of Superheating on the Structure and Physical Properties of Structural Alloy Steels" by A. Schöberl and R. Mitsche.[1] The influence of superheating of the melt is recognised in the case of cast iron and certain non-ferrous alloys. Piwowarsky was the first to describe the refining effect of superheating on the graphite size and the accompanying improvement in the strength properties. O. von Keil, R. Mitsche, A. Legat and H. Trenkler[2] found both in the laboratory and in works melts that the mode of solidification of cast iron was dependent on submicroscopical finely divided particles of silicates,

to which they gave the name of the "slag cloud" (though the term "slag" was intended to signify non-metallic inclusions generally), and of which the amount and distribution can be altered appreciably by the degree of superheating of the melt. One of the authors, Dr. R. Mitsche, contributed a paper on "The Flotation of Non-metallic Inclusions in Molten Metals" to the Carnegie Scholarship Memoirs of the Iron and Steel Institute in 1934. In this he dealt with cast iron and with aluminium alloys (silumin) and further developed the "slag cloud" theory. The metallic melt was considered to contain two sorts of nuclei :

(1) Intrinsic nuclei, which include metallic crystal residues which have not yet melted, or metallic crystals introduced into the melt from outside ; and

(2) Extrinsic (or foreign) nuclei of a non-metallic nature (the "slag cloud").

Both kinds of nuclei are strongly influenced by superheating. The intrinsic nuclei can dissolve, though new ones may be formed by additions to the melt. The extrinsic nuclei may coalesce, or may be reduced in a melt containing carbon, or increased by oxygen absorption, or otherwise altered by reaction between slag and metal. It is thus to be expected that superheating in steel may have a considerable influence. According to Eilender[3] and his co-workers, superheated molten steel gave material which, for the same tensile strength and yield point, showed somewhat better elongation and reduction of area and a considerably higher impact figure than usual, and its tendency to temper brittleness was stated to be less. Moreover, the superheated structural steel was less susceptible to welding cracks and flakes.

The first part of Schöberl and Mitsche's work was carried out on a number of experimental melts, made in the basic electric arc furnace and in the acid-lined high-frequency furnace, of nickel-chromium case-hardening steel containing about 0·17 per cent. carbon, 3·5 per cent. nickel, and 0·8 per cent. chromium. In the basic electric furnace a 50-kilo. melt was made in the normal way and cast after deoxidising. Then a second melt was made, deoxidised, and superheated. In both cases the same aluminium addition was made to the ladle. In the acid-lined high-frequency furnace a 150-kilo. melt was made, and, after deoxidising, half the melt was cast and the other half superheated. In this case also the same amount of aluminium was added to both ladles. All were cast into round chill moulds under similar conditions of casting and solidification, so that the influence of superheating alone should be predominant. Sections from the top, middle, and bottom of the ingots were examined. Temperatures were measured by an optical pyrometer and are given as uncorrected. Though too low, they give the necessary comparative information. Thus, all casting temperatures were between 1420 deg. Cent. and 1455 deg. Cent., the melts not superheated probably did not exceed 1460 deg. Cent., and the superheated melts varied from 1540 deg. to 1640 deg. Cent. (uncorrected). The casts of steel which had not been superheated showed the usual border of columnar crystals with equiaxial crystals in the central region. Superheating to 1550 deg. (basic) or 1540 deg. and 1570 deg. (acid) had no evident effect on the primary structure. After superheating to 1600 deg. (acid) there was an appreciable reduction of the columnar crystal formation ; after 1630 deg. (basic) it had almost disappeared. Thus it was concluded that superheating to 1640 deg. of melts made with either acid or basic lining will cause the almost complete disappearance of columnar crystals in ingots cast at the normal temperature.

The relation between primary and secondary structure is not sufficiently well known to enable any deductions about secondary structure to be made from the foregoing observations. The steels were therefore examined after being annealed at 720 deg., 820 deg., and 1020 deg. Cent., and slowly cooled. The results do not appear to have been very consistent. In the superheated acid steel the secondary structure was somewhat coarser than normal, and in the superheated basic steel more uniform and finer. After reduction of cross section in the ratios 4 : 1 and 40 : 1 by forging, and subsequent annealing at 800 deg. Cent., no essential difference was noted between any specimens, but after annealing at 900 deg. Cent. most of the superheated steels showed a larger grain size. These forged and annealed specimens were used for tensile and notched bar tests, the test pieces being taken from the outside of the larger bar while the whole section of the smaller bar (20 mm. diameter) was employed on the tensile test piece. No numerical results are given, but it is stated that there was, in individual instances of superheating, a certain improvement of elongation, reduction of area and impact figure, but that in others no difference was observed. The steels which had undergone the greatest reduction showed higher strength and lower ductility values, a result attributed not to the additional work they had received but to the difference in the rate of cooling of the different sized bars from the annealing temperature.

The forged steels were also carburised for eight hours at 850–870 deg. Cent. In basic melts no difference in grain size was observed ; in acid melts the superheated steel had a definitely smaller grain size. There was no difference in depth of penetration, but the transition zone from carburised edge to core was rather more abrupt in all superheated steels. Though an abrupt transition zone is generally considered undesirable, since it favours the production of internal stresses between case and core, the degree to which it was present in these specimens showed no detrimental effect in causing cracking or distortion in the course of forty successive hardening treatments applied to the specimen. It appeared clear from these experiments that, whereas superheating could exercise a strong refining action on the primary structure, the secondary structure and mechanical properties of the annealed material showed only a very slight degree of dependence on the primary structure and on the conditions as regards superheating of the melt.

Industrial melting, in an acid 6-ton arc furnace, of nickel-chromium-tungsten and nickel-chromium-molybdenum steels fully confirmed the effect of superheating to temperatures above 1600 deg. Cent. in producing a refining of the columnar cast structure, but no further study of the secondary structure or properties was made. It therefore still remains to be shown whether refining of the primary structure, produced in this way, has any practical importance. Kornfeld[4] showed that in normal material, forged and heat treated, for a given value of the tensile strength the region of equiaxial macrostructure is characterised by the highest elongation, reduction of area, and notched bar impact figure ; but this does not prove the utility of obtaining an extension of the equiaxial region by superheating. On the

other hand, Eilender, Walz and Meyer[3] claim an improvement in the life and behaviour of saw blades for wood cutting as a result of superheating the molten metal, combined, however, with other palliatives against the effects of lamination, such as repeatedly changing the direction of deformation of the blades during hot working. Schöberl and Mitsche recognise that it is the primary structure which is influenced by superheating. The secondary structure, both in the cast state and also after annealing, is not greatly affected. They are at present engaged in an investigation to determine whether it is possible by superheating the melt to refine the structure of steel castings to such a degree as to enable annealing to be dispensed with. The results of such a study are certain to be of interest, but those whose view is that the mechanical properties of a steel casting are determined far more by its secondary than by its primary structure, will not expect it to lead to any very revolutionary change in steel foundry practice.

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[2] *Archiv Eisenhüttenwesen*, 1933–34, 7, 579.
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[4] *Stahl und Eisen*, 1937, 57, 870; see THE METALLURGIST, October, 1937, 11, 74.

Heat of Formation of Alloys.

DIRECT measurements of the heats of formation of alloys have until recent years rarely been attempted, but indirect methods have often been applied. These consist of preparing the alloy and comparing the heat developed when the alloy in question is dissolved in a suitable solvent with that which would be evolved if appropriate quantities of the component metals were separately dissolved under the same conditions. The use of strongly acid media, such as dilute nitric acid, by early investigators led to erroneous results on account of the difference in the gaseous products of reaction.[1] Reagents such as a bromine-potassium bromide solution were found to be preferable for use with copper alloys.[2] The best of the early calorimetric work of this kind was that of Baker,[3] who examined the heat of formation of the copper-zinc alloys by dissolving them in aqueous solutions of ferric ammonium chloride and cupric ammonium chloride, and obtained indications of maxima in the heat-of-formation concentration curve at points corresponding to CuZn, Cu_2Zn_3, and $CuZn_2$. The most important of the more recent work is that of W. Biltz and his associates, published in a long series of papers entitled "Contributions to the Systematic Doctrine of Affinity" and dealing largely with evidence, based on heat of formation, for the existence of intermetallic compounds.[4] In these measurements the solution method was used, appropriate solvents being chosen for the individual systems of alloys under consideration; for example, bromine with potassium bromide was used for the copper-zinc alloys, hydrochloric acid for the cobalt-aluminium alloys, &c. This method is beset by many difficulties and possibilities of error. The heat of formation deduced from the experimental results is usually a relatively small difference between two fairly large heats of solution, that of the alloy and that of the separate metals.

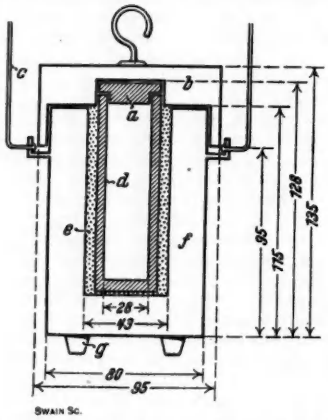

FIG. 1—*The Reaction Vessel. A=refractory lid, B=iron lid, C=handle for hanging the vessel, D=burnt refractory crucible, E=layer of sand, F=iron vessel, G=cork feet. (Dimensions in millimetres.)*

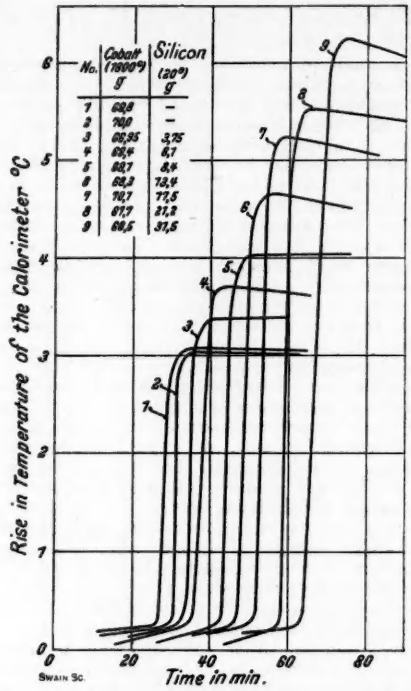

FIG. 2—*Rise in Temperature of the Calorimeter (Water Equivalent 7·58 ± 0·03 k.-cal.) After Pouring Cobalt on to Solid Silicon. Initial Temperature about 20·5 Deg. Cent.*

The direct method of determination of the heat formation has during the last few years been applied to a very wide range of alloys in Germany. The work originated at the Kaiser-Wilhelm Institute at Düsseldorf, and reports have been published from that Institute,[5] and also from the Kaiser-Wilhelm Institute for Non-Ferrous Metal Research at Stuttgart.

The general method employed was described in the first of these publications. The apparatus was the same as that previously used by Körber and Oelsen in their work on the iron-silicon alloys.[7] The reaction vessel is shown in Fig. 1. The crucible *d* is made of various materials according to requirements. Graphite served for aluminium, zinc, antimony, and copper alloys. Crucibles of siliceous material were used for iron, nickel, cobalt, and silicon. In determining the heat of formation of the first series of alloys mentioned in Part I, the cobalt-silicon alloys, a constant amount of 70 grammes of molten cobalt, deoxidised with manganese (0·2 per cent.) at a temperature of 1600 deg. Cent., was poured into the reaction chamber, which contained varying amounts (up to 32 grammes) of broken fragments of silicon. After the lids had been closed down the whole apparatus was immersed in a large calorimeter holding 6·3 litres of water and having a water equivalent of about 7·5 kilogram-calories. The cooling of the melt was very rapid and in the course of about three minutes the reaction vessel was opened to admit water, which then quickly reaches uniform temperature. A series of curves showing the rise in temperature of the calorimeter is shown in Fig. 2. The formation of alloys with more than 50 atoms per cent. of silicon could not be brought about in this way. For the silicon-rich alloys it was necessary to melt the silicon and pour it over solid cobalt. From the rise in temperature in the calorimeter the heat of reaction per gramme atom was calculated and the results plotted against concentration and compared with the indications of the equilibrium diagram. The values for the silicon alloys of iron, cobalt, and nickel are shown in Fig. 3, and illustrate the stability of the alloys corresponding to FeSi, CoSi, and in the case of nickel, Ni_2Si.

The aluminium alloys of these elements gave interesting results. They could not be made by pouring the molten metal over solid aluminium, as the aluminium floated and did not properly melt until the iron or other addition had solidified. The molten metals were therefore poured into molten aluminium, in which circumstances the reaction began at once. The heats of formation of the aluminium series of alloys shown in Fig. 6 are exceptionally high. This is particularly true of the cobalt and nickel alloys with aluminium, corresponding to CoAl and NiAl, compounds which have a very much higher melting point than their constituent metals. In Part II[5] several ternary systems of alloys are dealt with, including the iron-nickel-aluminium series, which have attained great importance since the discovery of the nickel-aluminium permanent magnet steels. They were investigated by pouring thoroughly deoxidised mixtures of iron and nickel in various proportions over molten aluminium. The heat of formation diagram is characterised by a ridge of high values running from FeAl to NiAl, which shows the maximum value of the system. Connection between heat of formation and magnetic properties in this series is not very striking, but the alloy which

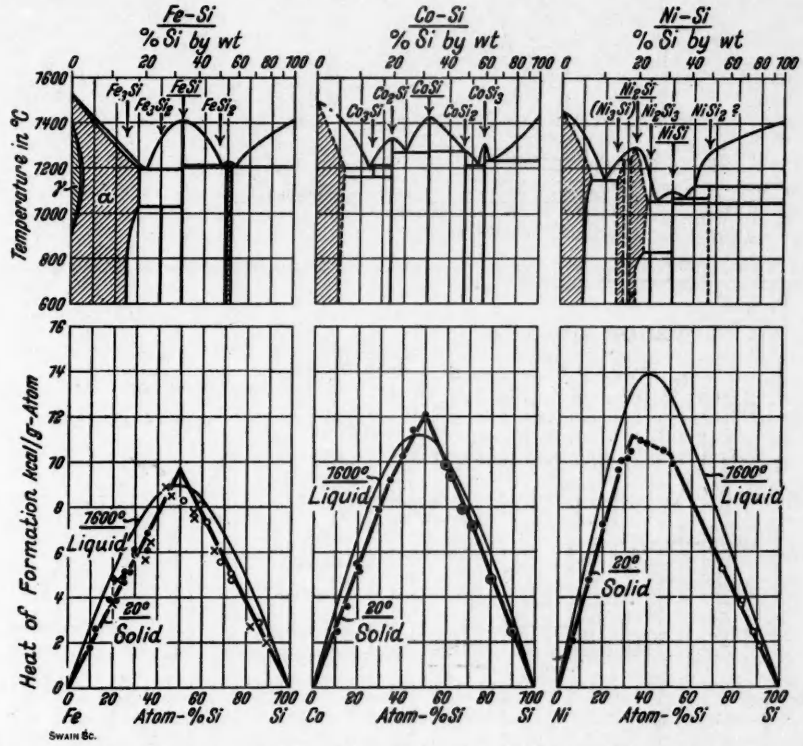

FIG. 3—*Constitutional Diagrams and Heats of Formation of Alloys of Silicon with Iron, Cobalt, and Nickel.*

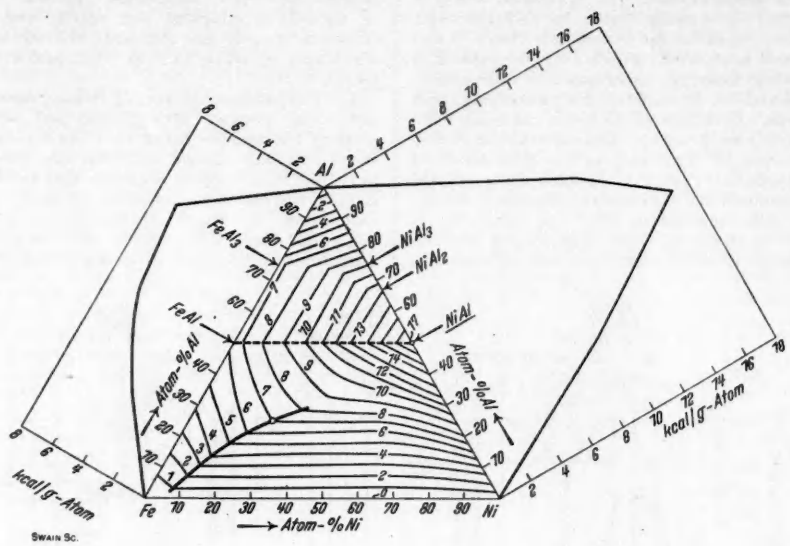

FIG. 4—*Heats of Formation in K.-Cal. per Gr. Atom of the Ternary Alloys of Iron, Nickel, and Aluminium.*

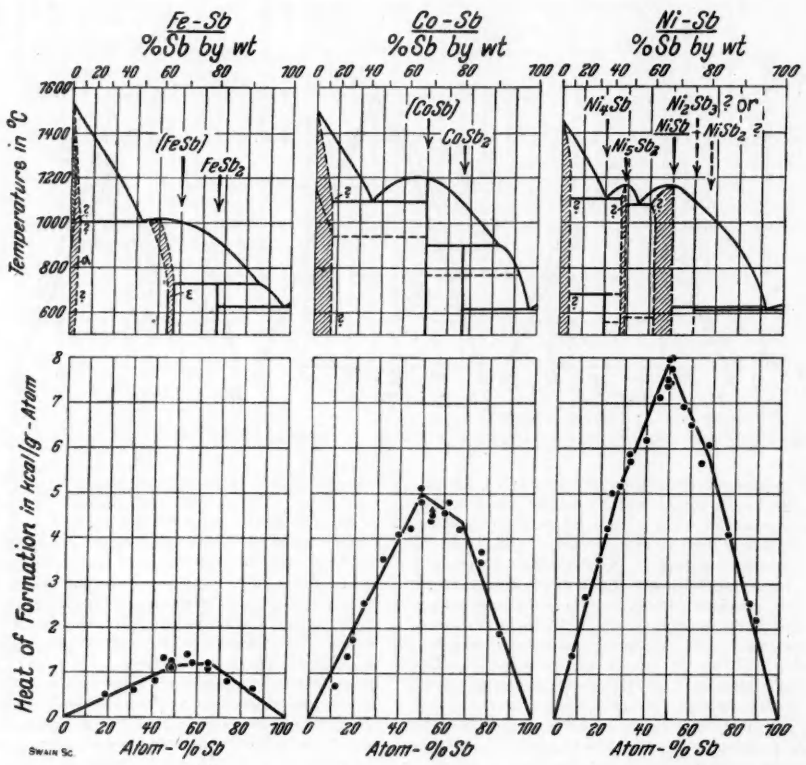

FIG. 5—*Constitutional Diagrams and Heats of Formation of Alloys of Antimony with Iron, Cobalt, and Nickel.*

is said to have the highest coercive force among the iron-nickel-aluminium alloys (atomic ratio 2 : 1 : 1) lies on a secondary ridge of high heat of reaction (Fig. 4). Similarly, in the copper-manganese-aluminium system the ferro-magnetic alloy (atomic ratio 2 : 1 : 1) showed considerably less than the maximum heat of formation of the series, but could be distinguished by a kink in the curve.

In Part III[5] further data are communicated with reference to binary alloys, chiefly non-ferrous. The alloys of nickel and antimony, like those of nickel and aluminium, show remarkably high values of heat of formation (Fig. 5). Among the tin alloys nickel-tin a number of indirect methods. The maximum value of heat of formation occurred at 60 atoms per cent. of zinc (Cu_2Zn_3).

The work at Stuttgart deals with alloys of lesser practical importance, but is nevertheless of considerable theoretical interest. For some of the lower melting point metals and amalgams the reaction vessel was of glass, melting had frequently to be done in argon, the apparatus was smaller (water equivalent 1·4 instead of 7·5 k.-cal.) and water could not be admitted to the reaction vessel. Certain regularities were observed in connection with the position of the elements in the periodic system ; for

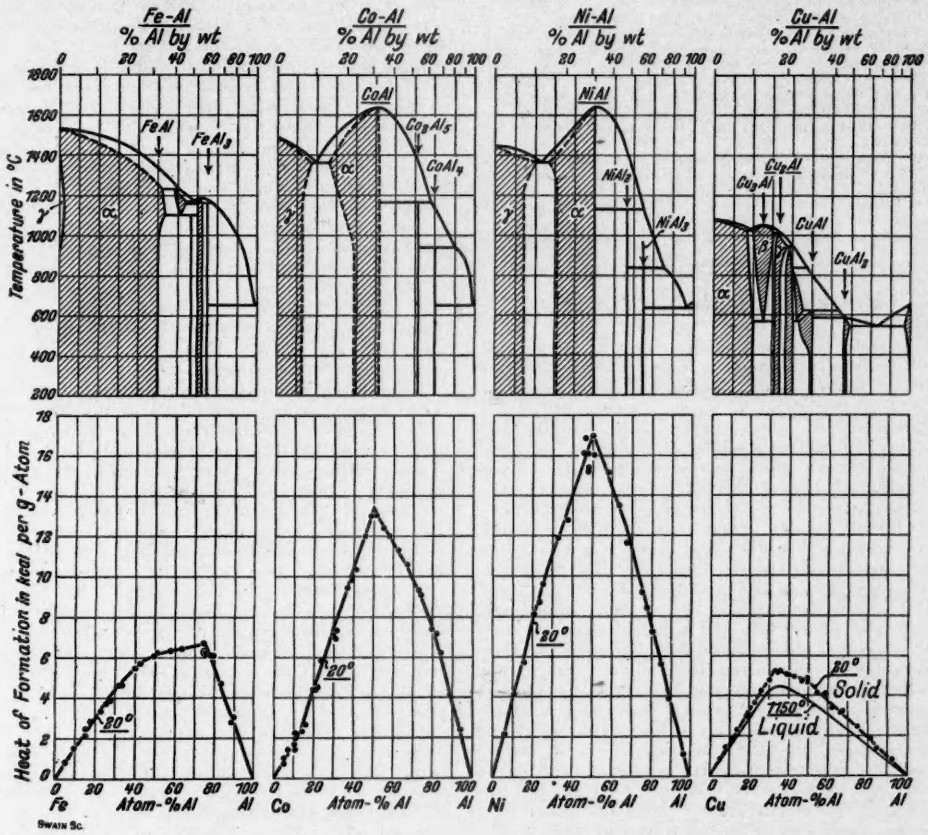

FIG. 6—*Constitutional Diagrams and Heats of Formation of Alloys of Aluminium with Iron, Cobalt, Nickel, and Copper.*

(maximum at 40–50 atoms per cent.) also showed much higher values than cobalt-tin (maximum at 50 atoms per cent.) or copper-tin (maximum at 25 atoms per cent.). The heat of formation when both metals were mixed in the liquid condition was much less, indicating at least in the case of cobalt and copper considerable dissociation of the compounds in the melt. The values for iron-tin could not be determined owing to immiscibility in the liquid condition. Some tests were made to redetermine the heat of formation of copper-zinc alloys to which a similar method had already been applied[9] and good agreement was shown to exist between the direct and example, in the alloys of bismuth, of tin, and of lead the maximum heat of formation decreased as the atomic weight of the second metal increased, *e.g.*, from lithium to sodium and magnesium. There was some correspondence also between a high difference in normal potential of the two elements of the binary alloy and a high maximum value of heat of formation.

The method of direct measurement of heat of formation has opened up a very wide field of investigation of a great variety of alloys, of which only a few typical examples have been referred to above. It may therefore be useful for further reference if, in

conclusion, a list is given of the alloy systems dealt with in the papers reviewed.

Reference.		Alloy system.
5 ...	(i) ...	Fe-Si, Co-Si, Ni-Si; Fe-Al, Co-Al, Ni-Al, Cu-Al; Zn-Sb.
	(ii) ...	Fe-Ni-Al : Fe-Co-Al : Fe-Al-Si : Cu-Ni-Al : Cu-Mn-Al.
	(iii) ...	Fe-Sb, Co-Sb, Ni-Sb; Fe-Sn, Co-Sn, Ni-Sn, Cu-Sn; Cu-Zn.
6 ...	(i) ...	Pb-Mg, Pb-Na, Pb-Li; Bi-Mg, Bi-Na, Bi-Li; Cd-Na.
	(ii) ...	Sn-Na, Sn-Li, Sb-Na, Sb-Li, Hg-Na.
8 ...	— ...	Sn-Bi, Pb-Sn, Pb-Sn-Bi, Pb-Cd, Pb-Ag, Ag-Zn, Cu-Zn, Cu-Ni, Fe-Ni.

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[3] T. J. Baker, *Phil. Trans.*, 1901, 196A, 529.

[4] A list of these papers and of others dealing with the indirect methods of determination of heats of formation is given by F. Körber, *Stahl und Eisen*, 1936, 56, 1401.

[5] "On the Thermochemistry of Alloys," Part I, by W. Oelsen and W. Middel, *Mitt. K.W. Inst. Eisenforschung*, 1937, 19, 1; Part II, by F. Körber, W. Oelsen and H. Lichtenberg, *ibid*, 1937, 19, 131; Part III, by F. Körber and W. Oelsen, *ibid*, 1937, 19, 209.

[6] W. Seith and O. Kubaschewski, *Zeit. Elektrochem.*, 1937, 43, 743; O. Kubaschewski and W. Seith, *Zeit. Metallkunde*, 1938, 30, 7.

[7] F. Körber and W. Oelsen, *Mitt. K.W. Inst. Eisenforschung*, 1936, 18, 109.

[8] H. O. von Samson-Himmelstjerna, *Zeit. Metallkunde*, 1936, 28, 197.

Books and Publications.

The Structure of Steel Simply Explained. By E. N. SIMONS and E. GREGORY. Small 8vo. Pp. x+115. 1938. London and Glasgow: Blackie and Son, Ltd. 3s. 6d.

THERE is a wide demand to-day for the popular presentation of the methods and results of scientific research, and this book on the structure of steel will be welcomed by many readers with technological interests. It owes its origin to a series of articles contributed by Mr. Simons to the *Edgar Allen News*, which is a well-known "house-organ" with a wide circle of appreciative readers. The book has as its object the enlightenment of people who "buy, sell, study, manipulate, and, in short, have to do with, steel," and any such reader will find that the story of the structure of steel is unfolded for him in an entertaining and straightforward manner, and is adequately illustrated with diagrams and photo-micrographs. A somewhat surprising omission is a description of the primary dendritic structure of the steel ingot, and its subsequent history in the forged product, though there is a brief reference to macrostructure. "To read a macrograph with accuracy," say the authors on page 75, "is not possible without considerable practice," and it must be confessed that "the typical macrograph" (Fig. 29) is not a very helpful initiation into the art. On the whole, the subject matter is clearly expressed, but the authors recognise that some of their explanations may carry the reader out of his depth. "The various constituents," they say (page 37), "are at first sight extremely confusing," and they fall back on a genealogical table, which shows sorbite as the parent of pearlite, in an endeavour to make things clear. Some of the confusion would not have arisen if the fundamental distinction between what Dr. Sauveur has called the "lamellar family" and the "granular family" had been recognised. Lamellar sorbite is a sister of pearlite, but granular sorbite is a cousin several times removed.

Mr. Simons in his preface goes further than is usual, even in popular books of science, in claiming that the text is "without inaccuracy or misstatement," and although this may be more an expression of confidence in Dr. Gregory than in what he modestly calls his own "piece of popular journalism," it is none the less a challenging statement which invites some examination. What, then, should be said about the information, given on page 87, that the critical volume change on heating a stainless steel is completed at 685 deg. Cent.? This, of course, is not correct, nor is it in accordance with the corresponding dilatometer curve (Fig. 34), which, moreover, is itself inaccurate in showing a pronounced change at 800 deg. Cent. in the rate of contraction of the γ-iron solid solution on cooling. But if the perfection claimed is not always reached, such inadvertent slips do not detract from the main value of the book, which certainly cannot fail to impress the reader with the significance of structure, and of the control of structure by variations of composition and heat treatment, in meeting the demands made on modern steel industry.

Dr. F. C. Lea, who contributes an Introduction, commends the book as an endeavour "to supply in a simple way the information that should be available to anyone interested in any industrial problem in connection with which some type of steel may be required to meet specific requirements," but, bearing in mind that a little learning is a dangerous thing, he wisely counsels all readers to consult the manufacturer before making technical use of their newly acquired information.

Elastic Properties of Non-ferrous Metals and Alloys: Collected Data. By J. MCKEOWN and E. D. WARD. 12in. by 9½in., 35 sheets. 1938. London: British Non-ferrous Metals Research Association. 6s.

THE authors, who are members of the staff of the B.N.F.M.R.A., have performed a valuable service in collecting, either from published work or from the Association's reports, information about the Young's Modulus, Limit of Proportionality, Elastic Limit (defined as "the maximum stress which a material will bear without showing any permanent deformation after the stress has been removed"), Proof Stress, and other characteristics of a large number of metals and alloys tested in tension.

Most of the data are given in the form of tables, but occasionally graphical representation is used. The metals and alloys have been divided into groups, and full details are given of their composition and condition as regards mechanical or heat treatment. The value of the compilation is increased by the indications given of the sensitivity of the strain-measuring apparatus employed. All information which failed to reach the high, but somewhat rigid, standard laid down by the authors was discarded. By exercising the critical faculty a little more freely a wider range of results might have been drawn upon with advantage, and some excluded even though they conform to the authors' standards. For example, it is not easy to believe that the Young's Modulus of one composition of duralumin, differently treated, can vary from 5·4 to 10·6 million pounds per square inch as recorded on Sheet 31, and such figures throw doubt on the limits of proportionality associated with them. Though the standards laid down by the authors have excluded some quite useful information while occasionally admitting data of doubtful utility, there is reason to suppose that all the most accurate values of the tensile elastic properties of the materials in question are included; and thanks are due to the authors for collecting them, a task which must have involved prolonged and careful study of the many sources of information, and to the Association for making the results accessible.